

## REPAIR OF ZIRCONIA-BASED THERMAL BARRIER COATINGS

### FIELD OF THE INVENTION

This invention relates generally to the field of materials and more particularly to  
5 ceramic thermal barrier coatings.

### BACKGROUND OF THE INVENTION

Thermal barrier coating materials are commonly used to protect underlying  
substrate materials from a high temperature environment. In modern gas turbine  
10 engines, hot gas path components formed of metal alloys such as nickel-based or  
cobalt-based superalloys are often coated with a layer of ceramic insulating material.  
Zirconia-based coatings, in particular 6-8% yttria stabilized zirconia (YSZ), is a material  
that is widely used for such applications. Zirconia may be deposited onto the substrate  
surface by a variety of processes, including for example plasma spray or physical vapor  
15 deposition (PVD). Plasma spray provides a coating formed of multiple overlapping  
splats of previously molten material. Physical vapor deposition provides a columnar-  
grained structure that may perform better than plasma sprayed coatings in certain  
applications due to an enhanced porosity control (lower thermal conductivity) and  
improved strain tolerance due to the inherent directionality of its structure (improved  
20 thermal shock performance).

Methods for repairing damaged ceramic thermal barrier coatings are known.  
United States patent 5,723,078 describes the use of a plasma spray process to repair a  
columnar-grained coating. The extremely high temperatures produced during a plasma  
spray process, as high as 15,000°C. for example, necessitate that such repairs be  
25 performed in a shop environment following disassembly of the machine containing the  
component to be repaired. United States patent 6,413,578 describes the use of a  
ceramic paste that can be applied to a damaged gas turbine component while the  
component remains installed. The paste includes a ceramic powder and a binder  
material that is thermally reacted to form the repair. Such chemically bonded repair  
30 materials generally do not perform as well as the original coating material, especially  
under conditions of cyclic thermal exposures.

United States patent 4,588,655 describes a ceramic coating consisting of alumina and zirconia particles, and United States patent 5,059,095 describes applying a dense coating of this material to a gas turbine rotor blade tip using a high velocity oxy-fuel (HVOF) process. The dense layer of alumina-zirconia material is useful for a gas turbine blade tip application due to its friction and abrasion qualities.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic illustration of a portable low velocity oxy-fuel tool being used to deposit a ceramic coating on a surface of a component that is in its operating position in a machine.

FIG. 2 is a partial cross-sectional illustration of a ceramic coating obtained by depositing a relatively low melting point powder and a relatively high melting point powder using a low velocity oxy-fuel process.

## DETAILED DESCRIPTION OF THE INVENTION

The present inventors have found that prior art coatings of alumina and zirconia applied by thermal processes such as air plasma spray (APS) or high velocity oxy-fuel (HVOF) have a life expectancy that is less than that of zirconia coatings not containing alumina due to spalling caused by the differential thermal expansion between the zirconia and the alumina. Furthermore, the thermal conductivity of such coatings is higher than that of pure zirconia coatings. An improved coating is described herein as combining zirconia (unstabilized or stabilized) with a material having a coefficient of thermal expansion and/or a thermal conductivity that is closer to that of zirconia than the corresponding property of alumina. The coefficient of thermal expansion of the material that is mixed with the zirconia may be within 30% of that of the zirconia in one embodiment, or within 20% or 10% of that of the zirconia in other embodiments. The thermal conductivity of the material may be no more than that of the zirconia in one embodiment, or no more than 20% higher than that of the zirconia in another embodiment. The coefficient of thermal expansion may be an important variable in the selection of the mix material in applications where coating life is a primary concern. In applications where thermal protection is a primary concern, the thermal conductivity may become a more important consideration to be balanced against coating life. The

mix material combined with zirconia advantageously has an incipient melting point sufficiently low so that particles of the material are at least partially melted during a low velocity oxygen fuel (LVOF) process so that the combined particle mix may be applied to a component of a machine such as a gas turbine by using LVOF equipment. The low velocity oxygen fuel process may be an oxy-acetylene flame spray (OFS), for example, or it may be a low velocity oxy-fuel process that utilizes hydrogen or other fuel.

The coefficient of thermal expansion ( $10^{-6}/^{\circ}\text{K}$ ), thermal conductivity (W/mK) and melting point ( $^{\circ}\text{C}$ ) of 8% yttria stabilized zirconia (8YSZ), alumina ( $\text{Al}_2\text{O}_3$ ), calcium titanate ( $\text{CaTiO}_3$ ), strontium titanate ( $\text{SrTiO}_3$ ) and sodium-zirconium-phosphate-silicate (NZPS) are as shown in Table 1. NZPS is a family of materials that can have several different stoichiometries. The values provided in Table 1 are for the specific combination of  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ , although other stoichiometries of NZPS are included within the scope of the present invention.

TABLE 1

MATERIAL	COE $10^{-6}/^{\circ}\text{K}$	conductivity W/mK	MP $^{\circ}\text{C}$
8YSZ	12.0	2.0	2,700
$\text{Al}_2\text{O}_3$	$\sim 8.0$	$\sim 30$	2,100
$\text{CaTiO}_3$	$\sim 14.0$	4.4	1,975
$\text{SrTiO}_3$	$\sim 11.4$	2.3	2,080
NZPS	$\sim 6$	1.75	1,275

Both calcium titanate and strontium titanate exhibit coefficients of thermal expansion that are closer to that of zirconia than that of alumina. The thermal conductivities of these materials are also close to that of the zirconia, especially when compared to the thermal conductivity of alumina, which is much higher than (an order of magnitude higher than) that of zirconia. The melting points of these materials are all lower than that of alumina and are sufficiently low so that particles of these materials that are delivered by a low velocity oxy-fuel process will be completely or at least partially melted to a degree sufficient to allow the materials to be effectively applied by this process.

FIG. 1 illustrates a low velocity oxy-fuel system 10 being used to spray a composite powder 12. The composite powder 12 may include a first constituent 14 that is a relatively high melting point ceramic material that normally cannot be applied with a LVOF process, for example either stabilized or unstabilized zirconia. The composite powder 12 also includes a second constituent 16 that is a relatively low melting point ceramic material that can be at least partially melted or fully melted and successfully applied by a LVOF process, for example calcium titanate or strontium titanate. The two constituents are mixed together to form a homogeneous mixture prior to spraying, such as by ball milling or by wet chemical mixing. The portion of the composite powder 12 that is the low melting temperature material may range from less than or at least 20 vol.% to 40 vol.%, or more, of the composite powder 12. While the proportions may vary for different materials and application temperature ranges, for the specific application of a gas turbine hot gas path component, the proportion of low-melting component will generally fall within the range of 20-40 vol. %. Particle sizes may be selected to ensure the proper operation of the LVOF system 10, such as in the range from -120 +325 mesh, from -140 +325 mesh, or from -150 +325 mesh for example.

Prior art low velocity oxy-fuel processes have not been used successfully to deposit zirconia due to the high melting point of zirconia. The prior art thermal spray processes used to apply zirconia coatings have included high velocity oxy-fuel (HVOF) and plasma spray. These processes are not useful for in-situ repairs of machines such as gas turbines due to the high temperature, high particle velocity, and/or high sound energy levels produced. The Figure illustrates a damaged region 18 of an existing coating 20 on a component 22 being repaired by the deposition of a repair coating 24 with the component 22 in place in its operating position within a machine of which it forms a part. Access is provided to the damaged region 18 without removing the component 22 from the machine. The damaged region may be cleaned with any known cleaning process, such as by grit blasting or chemical cleaning. The repair coating 24 may be applied onto the substrate 22, onto a bond coat layer (not shown) covering the substrate 22, or onto a portion of the existing coating 20. Repair coating 24 may be applied to any desired thickness, such as in the range of 8-35 mils, for example.

The coefficient of thermal expansion of sodium-zirconium-phosphate-silicate is lower than that of alumina. However, NZPS does exhibit a thermal conductivity that is

lower than that of both alumina and zirconia, and it also has the lowest melting temperature of the materials described above. NZPS may be selected as the low-melting temperature powder 16 for applications where thermal conductivity is especially important.

5           One may appreciate that it is possible to use a LVOF process to apply a variety of relatively high melting temperature ceramic powders 14 that are normally not successfully applied with LVOF by combining the high melting temperature powder 14 with a low melting temperature powder 16 in the LVOF process. A typical cross-section of the resulting coating 24 is illustrated in FIG. 2. The lower melting temperature  
10       constituent 16 has been at least partially melted by the spray process and has re-solidified to form splats 26. The splats 26 surround and encase the unmelted or potentially partially melted particles of the high melting temperature material 14. Complete melting of the low melting temperature particles 16 is not necessary. Surface melting of the particles 16 is sufficient. It may be difficult to quantify a specific amount  
15       of melting because a number of variables can affect the coating microstructure. Test data may be useful for identifying an acceptable microstructure for a particular application. The two constituent particles 14, 16 will sinter during a subsequent high temperature heat treatment and/or during the subsequent operation of the component. The resulting coating 24 is relatively porous when compared to a plasma sprayed  
20       coating (typically 10-15% void fraction), with a typical void percentage being in the range of 20-25%.

          While various embodiments of the present invention have been shown and described herein, it will be obvious that such embodiments are provided by way of example only. Numerous variations, changes and substitutions will occur to those of  
25       skill in the art without departing from the invention herein. Accordingly, it is intended that the invention be limited only by the spirit and scope of the appended claims.